Quantum Coherence in Fe_8 Molecular Nanomagnets

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Abstract

We report observation of coherent quantum oscilations in spin-10 Fe_8 molecular clusters. The powder of magnetically oriented Fe_8 crystallites was placed inside a resonator, in a dc magnetic field perpendicular to the magnetization axis. The field dependence of the ac-susceptibility was measured up to 5 T, at 680 MHz, down to 25 mK. Two peaks in the imaginary part of the susceptibility have been detected, whose positions coincide, without any fitting parameters, with the predicted two peaks corresponding to the quantum splitting of the ground state in the magnetic field parallel and perpendicular to the hard magnetization axis.

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The high value of the spin, $S = 10$, in molecular clusters like Mn_{12} and Fe_8 allows to test the border between quantum and classical mechanics [1–3]. For a large spin, the transitions between degenerate spin levels appear in high-order of the perturbation theory on the spin-phonon, crystal field, dipole, hyperfine, and other interactions. This results in a long lifetime of spin states and produces a fascinating opportunity to study the quantized spin levels and transitions between them in macroscopic magnetization measurements [4–10]. Owing to a large anisotropy, the classical magnetic energy of the clusters in zero magnetic field has two symmetric minima separated by the energy barrier. From the classical point of view, the magnetic relaxation in Mn_{12} and Fe_8 crystals can be viewed as thermal activation over this barrier. However, when the temperature becomes small compared to the anisotropy energy, the relaxation is dominated by quantum tunneling under the barrier. The corresponding matrix elements arise from the terms in the Hamiltonian which do not commute with the equilibrium orientation of the spin [11–15]. If these terms are small, tunneling from the levels near the bottom of the barrier is negligible but tunneling at the top of the barrier may have a significant rate [15]. It has been firmly established experimentally for both Mn_{12} [21] and Fe_8 [10] that within a certain temperature range the tunneling from thermally populated spin levels is responsible for the magnetic relaxation. In Fe_8 the distance between the ground state level and the first excited spin level is about 5K. As the temperature is lowered well below that value, the populations of excited spin levels subside to exponentially small values and only transitions between the ground state levels become of practical interest [10]. By applying the external dc magnetic field one can adjust the rate of these transitions to the frequency of the ac field and observe coherent quantum oscillations of the spin, similar to the textbook example of ammonia molecule. For a macroscopic spin it has been attempted in antiferromagnetic particles of ferritin [16], while for a small spin the coherent oscillations have been reported in rare-earth ions glasses [17] and non-oriented $CrNi_6$ clusters [18]

Among systems which consist of well-characterized [19,10,20] identical nanomagnets Fe_8 has the highest spin and, therefore, the ac-susceptibility study of the quantum splitting of its ground state can be an important landmark in the search for macroscopic quantum

coherence. Besides its value for fundamental quantum physics, the observation of quantum coherence in molecular nanomagnets may also add them to the list of candidates for elements of quantum computers. In this letter, we report such an experiment at 680 MHz down to 25 mK on magnetically oriented Fe_8 grains in a static magnetic field perpendicular to the easy magnetization axes of the grains. The advantage of this configuration is the control of the tunneling rate by the magnetic field [21]. We have chosen Fe_8 over Mn_{12} because in Mn_{12} strong hyperfine fields split each molecular spin state into a few hundred levels closely packed into an energy band which is wider than the tunneling splitting Δ [22]. On the contrary, in Fe_8 the hyperfine fields are very weak in the majority of clusters and the resulting splitting of the molecular spin states remains within the limit $H_z < \Delta/2g\mu_B$ (g being the gyromagnetic factor).

Pure Fe_8 crystals of length ranging from less than 1μm to 2mm were synthesized according to Ref. [23]. The nominal composition, $(((C_6H_{15}N_3)_6Fe_8(\mu_3 - O)_2(\mu_2 - OH)_{12}(Br_7(H_2O))Br_8H_2O)$, was checked by chemical and infrared analysis. The matrix orientation of the crystals was performed by indexing 25 randomly searched reflections inside the Enraf-Nonius CAD4 X-ray diffractometer with graphite monochromated MoKα radiation. The measured crystall cell parameters, $a = 10.609(7)$, $b = 14.15(2)$, $c = 15.002(9)$Å, $\alpha = 89.45(9)$, $\beta = 10.03(5)$, $\gamma = 109.42(9)$ deg, are in accordance with published values [23]. The Mossbauer spectrum of the crystals, in accordance with the published data [19], evolves from an asymmetric paramagnetic doublet at room temperature to three magnetic hyperfine sextets below 4 K. This corresponds to the blocking of the trivalent Fe cations in three different crystallographic sites inside the spin-10 Fe_8 cluster.

Before carrying out the high-frequency experiments, we also performed the dc and ac magnetic characterization of our samples. Both, oriented single crystals and oriented powder, have been studied. The orientation of single crystals was done inside the Enraf-Nonius diffractometer, while the orientation of the powder was done by solidifying an epoxy (Araldit) with Fe_8 micrometric crystallites buried inside, in a 5.5 T field at 290 K during 12 hours. The data on both, single crystals and oriented powder, are similar to those obtained in

Ref. [10]. Below the blocking temperature, which depends logarithmically on the frequency of the ac-field, periodic steps appear in both, in-phase and out-of-phase, components of the susceptibility, with a period of 0.24 T. Fig. 1 shows the variation of the out-of-phase component of the susceptibility versus magnetic field at 500 Hz and 2 K.

To measure the magnetic susceptibility at high frequency, we used a split-ring resonator (also called loop-gap resonator) [24]. Its frequency resonance was around 680 MHz and its quality factor was 3100 at low temperature. Because the electric field exists in the gap and not in the loop, this resonator is particularly attractive for magnetic susceptibility measurements. The sample consisted of oriented Fe_8 micrometric crystallites imbeded in an epoxy slab. The total mass of the crystallites was 0.08 g. The external magnetic field was obtained from a superconducting magnet. The resonator was pressed against the wall of the mixing chamber of a ^{3}He-^{4}He dilution refrigerator. The steady magnetic field was applied perpendicular to the easy axis of the crystallites, whereas the ac field was parallel to the latter. This was important for having non-vanishing matrix elements between the two levels originating from the splitting of the ground state. To measure the magnetic susceptibility χ, the resonance line of the resonator with the sample inside was determined using electromagnetic pulses of low repetition rate (to avoid heating of the sample). The line shape was Lorentzian. The line broadering was proportional to the imaginary part of the susceptibility (χ") and the resonance frequency shift was proportional to its real part, (χ'). Fig.2 shows the variation of χ" as a function of the magnetic field for two temperatures. Two peaks are clearly present, the first one at $H_1 = 2.25 \pm 0.05$ T and the second one at $H_2 = 3.60 \pm 0.05$ T. The peaks at 25 mK have roughly the same heights as the ones at 200 mK. At higher temperature they broaden and disappear in the background noise. The two peaks also exist, though are much less pronounced, for the field parallel to the easy magnetization axis.

To the first approximation, the Hamiltonian of Fe_8 is [19,10]:

$$\mathcal{H} = -DS_z^2 + ES_x^2 - g\mu_B \mathbf{H} \cdot \mathbf{S} \tag{1}$$

Numerical diagonalization of this Hamiltonian with $D = 0.31$ K and $E = 0.092$ K (Ref. [19]) shows that at a $2-3$ T field, directed perpendicular to the z-axis, the splitting Δ of the two lowest states becomes of the order of a few tens of mK, which limits H_z by a few Gauss if one is to look for the quantum coherence (the frequency of our resonator correponds to an energy $\hbar\omega = 32$ mK). The dipole fields can, in principle, be greater. However, in the oriented zero-field-cooled sample the numbers of spin looking "up" and "down" are equal. Statistically, about 1/8 of molecules must be sensing zero dipole field. The more "dangerous" H_z field is coming from the impossibility to apply the external field exactly perpendicular to the easy axis. The above limitation on the longitudinal field would require the accuracy in the orientation of the Fe_8 crystal with respect to the magnetic field better than $H_z/H_x \sim 10^{-4}$ rad, which is difficult to achieve. For that reason, despite having at our disposal large single crystals of Fe_8, we chose to work with the oriented powder of Fe_8 crystallites. If the orientations of the grains are within a cone of 0.1 rad, which is possible to achieve, the 10^{-6} fraction of the sample, that is to say a macroscopic number of Fe_8 clusters, will satisfy the resonance condition. To see the corresponding resonance in the ac-susceptibility measurements, the frequency of the ac-field must equal $\Delta/\hbar$, which, for the above numbers, corresponds to a few hundred MHz.

The above frequency must be greater than the frequency of the absorption and emission of phonons, or other excitations, by the magnetic clusters, otherwise the coherence will be destroyed. Although little is known about the interaction of the clusters with the environment, it is believed that at low temperature they are in the underdamped regime [26]. In that regime the frequency in question is the pre-exponential factor (the attempt frequency) of the tunneling rate. According to Ref. [10], in Fe_8 this frequency is about 30 MHz.

When the field is applied perpendicular to the easy axis, the splitting Δ depends on the magnitude of the field H and its angle ϕ with the hard axis. The dependence of Δ on H, for different values of ϕ, obtained by the numerical diagonalization of the Hamiltonian (Eq. 1) using $D = 0.31$ K and $E = 0.092$ K, is plotted in Fig. 3. The insert shows $\Delta(\phi)$ for a fixed value of H. The pronounced minima at $\phi = 0$ are due to the non-Kramers topological

quenching of tunneling noticed by Garg [27]. In the absence of dissipation, the contribution of each Fe_8 crystallite to the imaginary part of the susceptibility χ" is proportional to $\delta(\omega - \Delta)$. At a given H, the total χ" is then proportional to

$$\int_0^{\pi} g(\phi)\delta(\omega - \Delta[\phi, H])d\phi, \tag{2}$$

where $g(\phi)$ is the distribution of crystallites over ϕ. Since no preferred orientation on the angle ϕ is expected, the integral in Eq.2 is proportional to $|\partial\Delta/\partial\phi|^{-1}$. Now, we can notice that according to the inset of Fig. 3 the derivative of Δ over ϕ equals zero at $\phi = 0$ and $\phi = \pi/2$. Therefore, we conclude that χ"(H) must have two peaks, which are solutions of the equations:

$$\begin{aligned} \Delta(\tfrac{\pi}{2}, H_1) &= \omega \\ \Delta(0, H_2) &= \omega \end{aligned} \tag{3}$$

where $\omega = 2\pi f$ and f is the frequency of the ac field. That is, the two resonance peaks we have experimentally observed correspond to the quantum splitting of the ground state for the cases when the field is perpendicular and parallel to the hard axis. From the positions of these two peaks, we have extracted the values $D = 0.275 \pm 0.005$ K and $E = 0.092 \pm 0.005$ K of equation 1. These values are in remarkable agreement with the data given by other authors [19,10,20]. It remains to be explained, however, why the same two peaks of much lower intensity appear in the field parallel to the easy axis (Fig.2). In our opinion, this must be due to the non-perfect orientation of the crystallites. If the orientation is done below 9T, there is always a small fraction of the crystallites perpendicular to the field independently of its direction [25]. It should also be mentioned that we have not observed either spin echoes or the non-linear dependence of the susceptibility on the power of the ac field [17]. This can be due to very short relaxations times. Indeed, the large non-resonant magnetic susceptibility suggests a large number of non-resonant magnetic moments which should give spectral diffusion and, thus, reduce efficiently the relaxation time of the resonant Fe_8 clusters.

The classical two states for which we observe the coherence are two symmetric **S** states at some angle with the applied dc field, shown in the insert to Fig.4. Numerically, we find that

the classical barrier height vanishes at H_{min} that depends on the angle betwen the field and the hard axis. This dependence has two extrema: $H_{min} = 3.34T$ and $H_{min} = 4.71T$, which roughly have the same ratio as the two experimental peak values. However, the experimental peaks are located at 2.3 T and 3.6 T, where the barrier still has the height of about 3 K, much higher than the experimental temperature. It is also instructing to show quantum states which exhibit quantum coherence. The gap Δ separates the first excited state $|1>$ from the ground state $|0>$. Each of these states can be written as a superposition of the eigenstates $|m>$ of S_z:

$$|0>=\sum_{m=-10}^{m=10} A_m|m>, |1>=\sum_{m=-10}^{m=10} B_m|m> \ . \tag{4}$$

Here $A_m = A_{-m}$ while $B_m = -B_{-m}$. Fig.4 shows $|A_m|^2$ and $|B_m|^2$ for the first resonance, $H = 2.25T$, as functions of m for $-10 < m < 10$. These are quantum counterparts of classical canted spin states shown in the insert.

To conclude, we have observed coherent quantum oscillations in spin-10 Fe_8 molecular clusters. The two observed susceptibilty peaks are expected from the biaxial system of particles oriented along the easy axis but radomly distributed with respect to the orientation of their hard axes. The quantum coherence explanation provides a remarkable agreement between the parameters D and E of the Hamiltonian deduced from our experiment and those previously reported.

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FIGURE CAPTIONS

Fig. 1. Periodic steps in the out of phase low-frequency ac-susceptibility of Fe_8 due to resonant spin tunneling, at 500 Hz and 2 K.

Fig. 2. Dependence of the imaginary part of the high-frequency ac-susceptibility of Fe_8 as a function of transverse magnetic field. The dashed lines indicate the peak locations H_1 and H_2 obtained from the Hamiltonian using the parameters $D = 0.31$ K and $E = 0.092$ K. The solid circles are obtained with the magnetic field parallel to the easy axis. For clarity, the curves are arbitrary translated vertically.

Fig. 3. Dependence of the ground-state splitting as a function of transverse field in Fe_8 for different orientations of this one in the plane perpendicular to the easy axis. The insert shows the angular dependence of the splitting at a fixed field.

Fig. 4. Probability distribution over m in the ground state and the first excited state, $|A_m|^2$ and $|B_m|^2$, respectively. The inset shows a double-degenerate classical ground state.

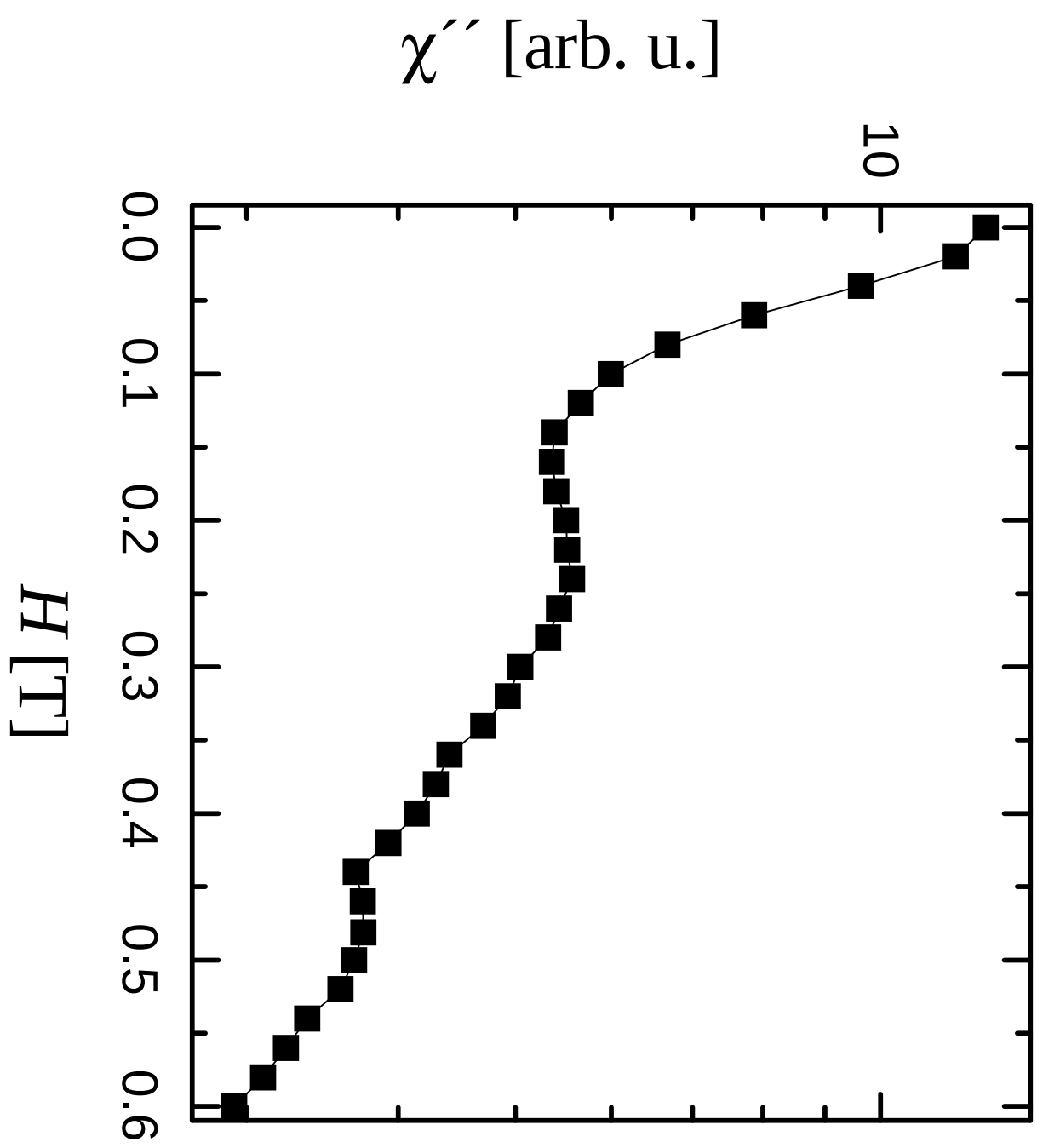
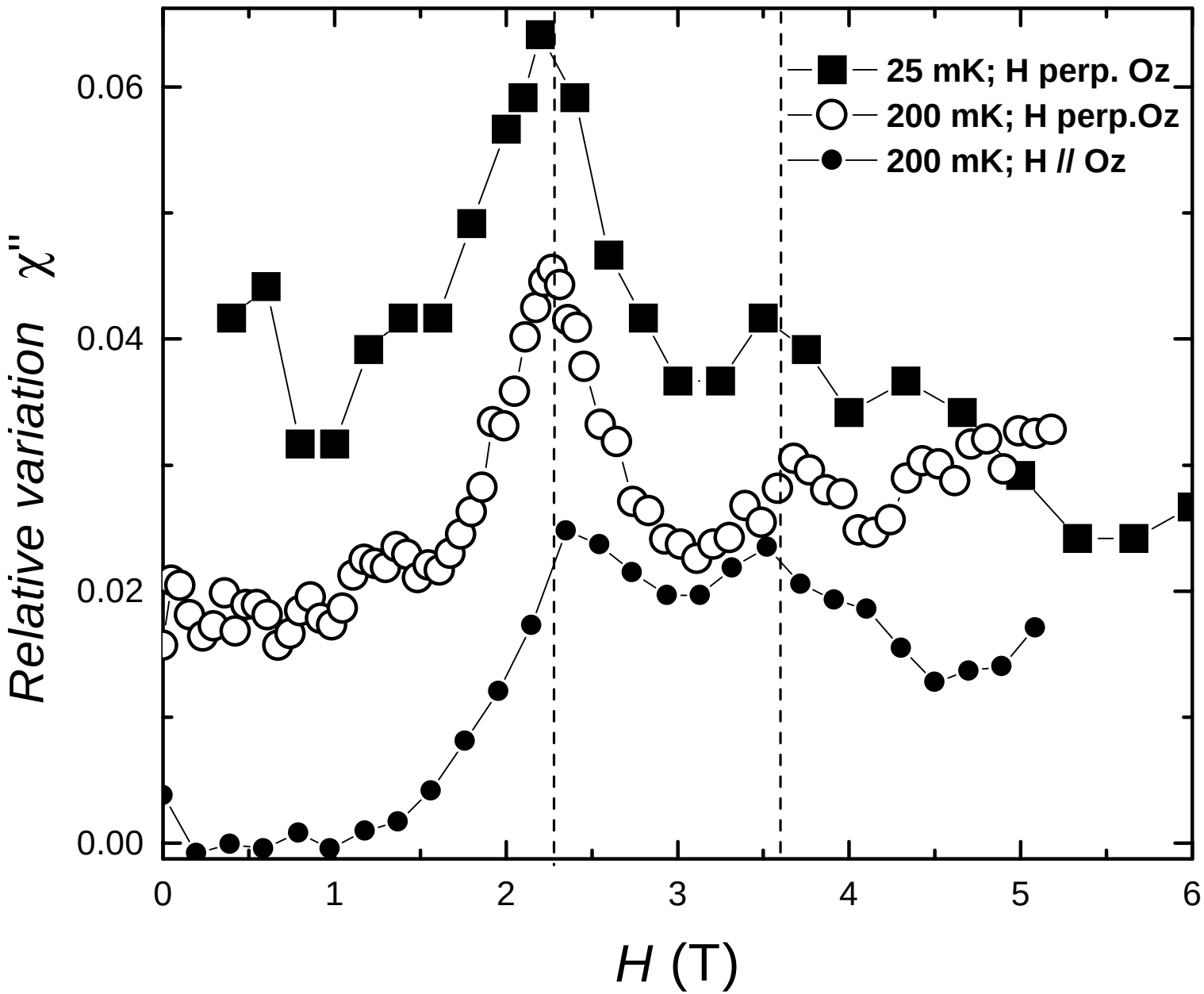


Figure 1 (E. del Barco *et al.*)

Figure 2 (E.del Barco et al.)



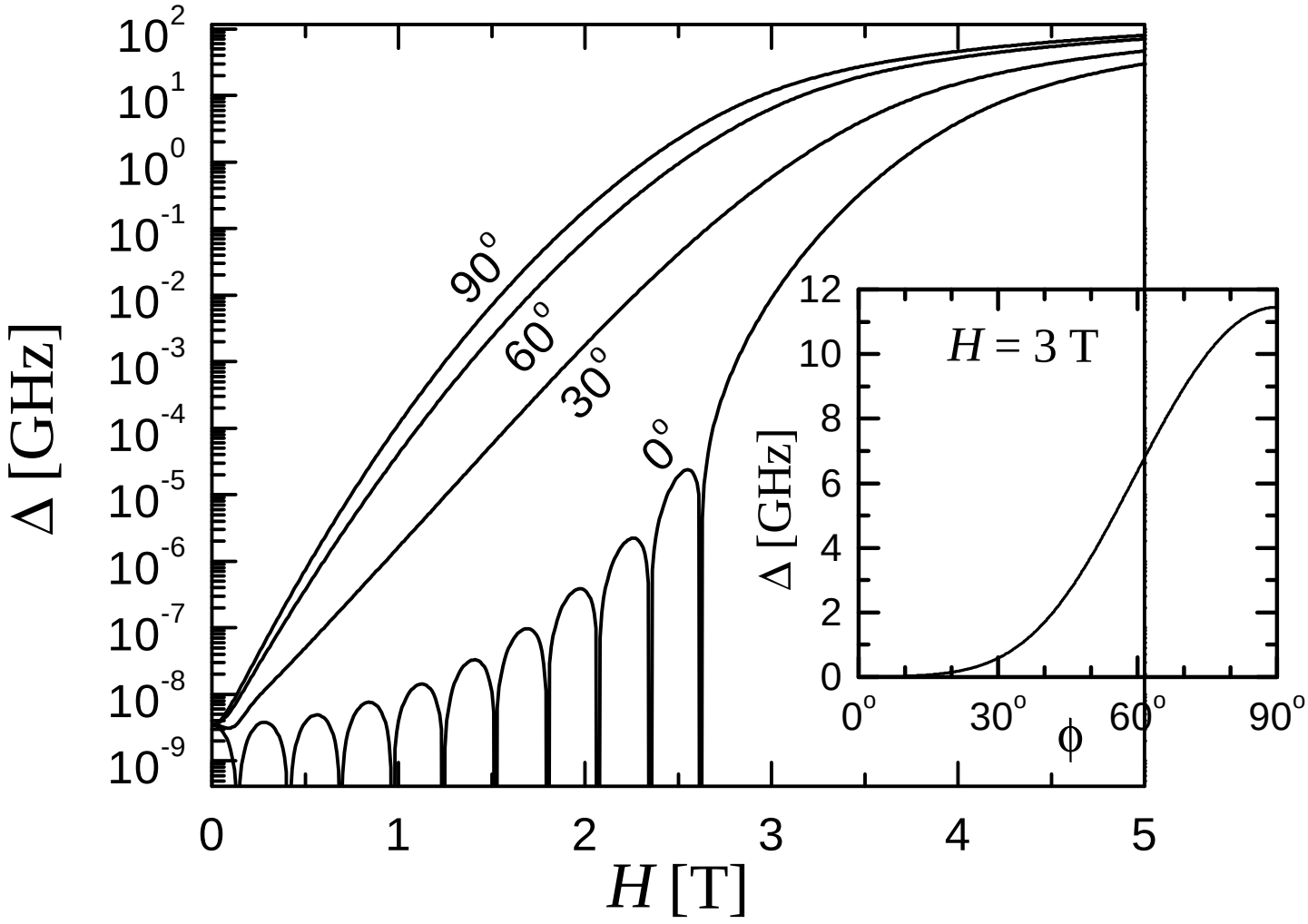


Figure 3 (E.del Barco et al.)

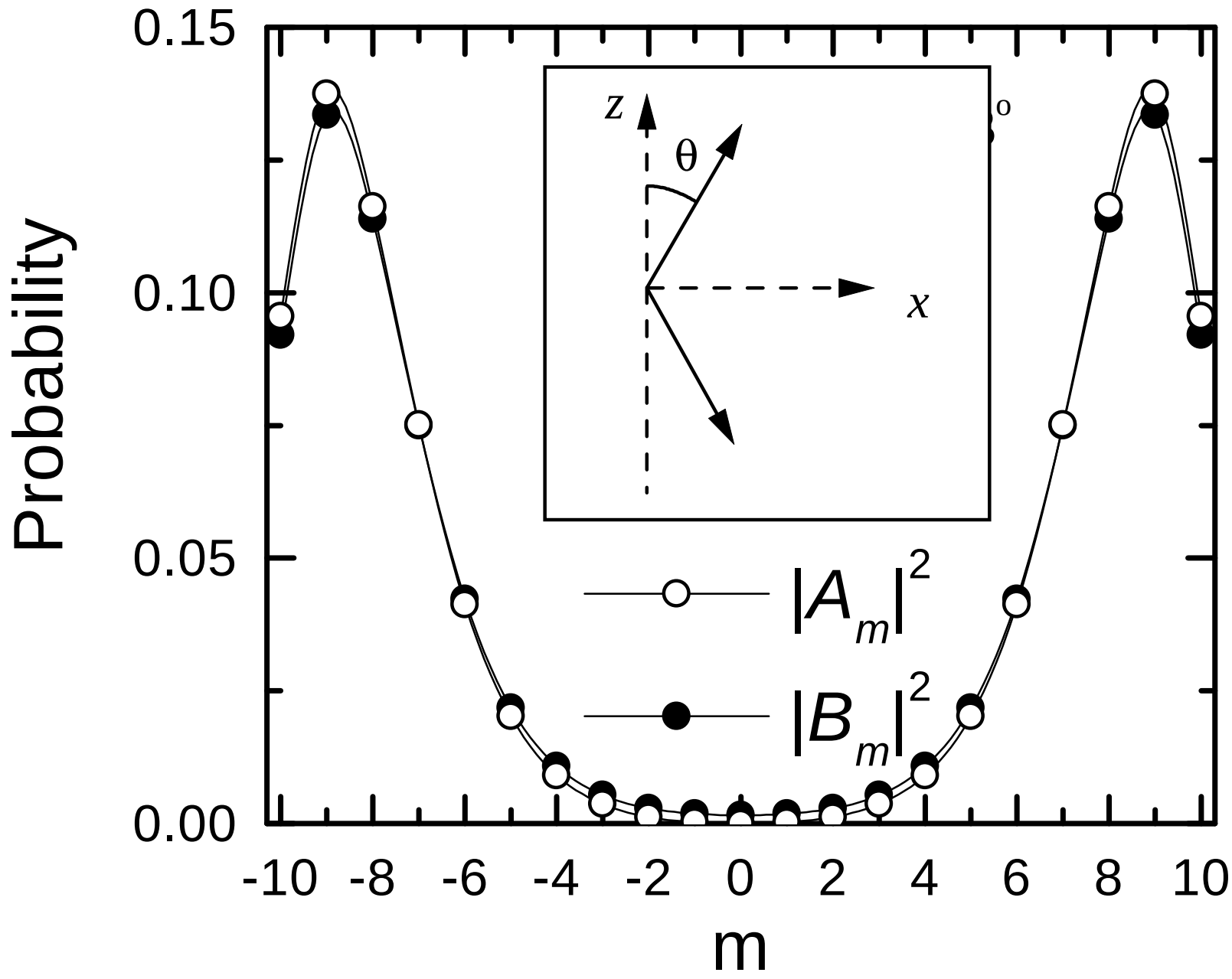


Fig. 4